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Effect of Motion of Impurity Ions on Electrical Properties of Polymer materials

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Abstract

In melt-crystallized polymers, free spaces with inhomogeneous size exist between crystallites. These free spaces results from non-crystalline polymer molecules which are not taken in into the crystallites. These free spaces become a path for impurity ions to move. The ionic motion along such path with the inhomogeneity affects the electrical properties of polymer materials. In order to study the effect of such ionic motions on energy loss, the interaction between ionic motion and inhomogeneous structure on the electrical properties was investigated. For this objective, the permittivity and the electric modulus were observed for isotactic poly(propylene) (iPP) and plasticized poly(vinyl chloride) with dioctyl phthalate (p-PVC) by means of the Broadband Dielectric Spectroscopy. A simple DC conduction is observed for p-PVC. However, for the iPP, another ionic motion appears on lower frequency side in addition to the DC conduction at high temperature. This change of ionic motion is considered to be caused by a phase transition in crystalline phase accompanied by a structural change in the non-crystalline part.

Keywords: ionic motion; isotactic poly(propylene); non-crystalline molecule; permittivity

1. Introduction

Residual ions getting mixed in polymers in manufacturing processes of polymers cause some sort of change in electrical properties of polymers. For example, they cause the water tree [1] which is one of the causes of the dielectric breakdown when the polymers are used as an insulator [2]. Furthermore, they

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cause some effect on electrical energy loss under an applied electric field to a polymer material. The origin of the electrical energy loss is an internal friction which is caused not only by an orientation motion of dipole of polymer but also by the ionic motion [3]. The interaction between the ions and the polymer molecules plays an important role in the electrical properties of polymers.

Most of polymers crystallize when they are cooled from a melt to a room temperature [3]. However, a relatively large amount of non-crystalline polymers exists between crystallites. This is a remarkable feature of polymer solid. In a part of the non-crystalline polymers, there are free spaces with various sizes. This inhomogeneity of free spaces results from a thermal motion of the polymer molecules with amorphous conformation. An ion moves through these free spaces. There are two types of the non-crystalline part in the crystallized polymers from a point of view of ionic motion [4,5]. One is the non-crystalline parts between crystallites. Another is the non-crystalline parts in a boundary region between aggregates of the crystallites. In the polymer crystallized from the melt, crystallites aggregate and make sphere shaped aggregation. The aggregate is usually called spherulite [3]. It is considered that the free spaces which exist in non-crystalline part compose a hierarchical structure of inhomogeneous ionic motion path composed by an inter-crystallite part and an inter-spherulite boundary.

In fact, an existence of plural kinds of motion of impurity ions is recognized in the low density poly(ethylene) (LDPE) crystallized from a melt [4,5]. It was also found that such kind of variety of ionic motions affects electrical properties of LDPE. A characteristic of DC conduction appeared at the loss permittivity in low frequency range is also caused by such ionic motions. Furthermore, similar result was also observed for the polyvinyl chloride-poly(1,4-cis-butadiene) blends (PVC-PBD) although it has a different kind of inhomogeneity [6].

Although a basic knowledge of the motion of the impurity ion is important for a research of the DC conduction in polymers, the study of such topic is hardly found in literatures. In this study, an effect of the interaction between the ionic motion and the inhomogeneous structure on the electrical property of polymer solid was studied. For this objective, the permittivity and electric modulus were observed for isotactic poly(propylene)(iPP) and plasticized poly(vinyl chloride) with dioctyl phthalate (p-PVC) by means of the Broadband Dielectric Spectropy (BDS). The permittivity and the electric modulus are useful physical quantities for the investigation of the ionic motion in inhomogeneous structure with free energy barriers [7]. Knowledge about the relation between the motion of the residual ions and polymer structure is important not only for a practical use of iPP and p-PVC but also for a basic understanding of the electrical properties of polymers

2. Experimental

Pellets of iPP which was given by Nissan Chemical Industry Ltd of Japan were melted at about 120°C. After the pellets were sufficiently melted, it was cooled down to the room temperature and the film of iPP was obtained. The sample of p-PVC was molded in kneading by a roller and after that it was shaped into a film by pressing. It was given by ZEON CORPORATION of Japan. A weight rate of dioctyl phthalate is 20 to 100 of poly(vinyl chloride). A thickness of both samples is 0.28mm. The samples of the iPP and the p-PVC are both commercial grade.

Electrical measurement was made by the apparatus of Schlumberger SI1260 Impedance/Gain-Phase Analyzer with an amplifier of Keithley428. At the frequencies lower than 10Hz, the amplifier of Keithley428 was used with the impedance analyzer. On the other hand, the amplifier was not used at frequencies higher than 10 Hz. The three-Terminal-Configuration Electrodes were used. The configuration of the apparatus is illustrated in Fig.1.

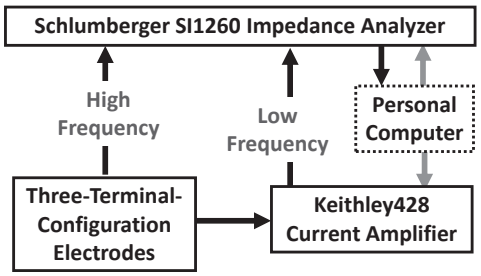

Fig. 1. Configuration of Apparatus of Electrical Measurement

3. Analysis

Electric modulus formalism is useful in order to investigate the ionic motion [7,8]. The electric modulus M^* is the frequency response function defined by a permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ as the following equation,

$$M^* = \frac{1}{\varepsilon^*} \tag{1}$$

Both of the electric modulus and the permittivity are functions of frequency. The electric modulus is also expressed by using a decay function $\varphi(t)$ as follows,

$$M^*(\omega) = M_s\left[1 - \int_0^\infty \left\{-\frac{d\varphi(t)}{dt}\right\} e^{-i\omega t} dt\right] \tag{2}$$

Here, ω is an angular frequency and M_s is equal to the inverse of the static limiting permittivity ε_s.

When the decay function is given by the Debye-type function,

$$\varphi(t) = e^{-\frac{t}{\tau}} \tag{3}$$

The Eq.(2) is written by a following equation,

$$M^* = M' + iM'' = M_s \frac{(\omega\tau)^2}{1+(\omega\tau)^2} + i M_s \frac{\omega\tau}{1+(\omega\tau)^2} \tag{4}$$

Here, τ is called the conductivity relaxation time [7]. It is identical to the ordinary relaxation time for dipole orientation. If the experimental result is in agreement with the Eq.(4), the ionic motion corresponds to a simple DC conduction characterized by the single conductivity relaxation time. Experimental results of this study are analyzed by the electric modulus formalism.

4. Experimental Results

4.1. p-PVC

Although many polymers are crystallized when they are cooled from the melt, poly(vinyl chloride) is one of the polymers which are slightly crystalline [3]. Furthermore, the microstructure becomes more homogeneous by adding dioctyl phthalate as a plasticizer. Therefore, in the sample of p-PVC, it is considered that the free space for ions to move is almost homogeneous. When the ions move in homogeneous free space under the electric field, a typically simple spectrum of permittivity is expected in a low frequency range.

The frequency spectrum of a loss permittivity ε'' observed by BDS is shown in Fig.2. The plot of a logarithm of the loss permittivity against a logarithm of the frequency f in Fig.2 shows a characteristic of the DC conduction. However, details about the diversity of the ionic motion are not clear from this plot.

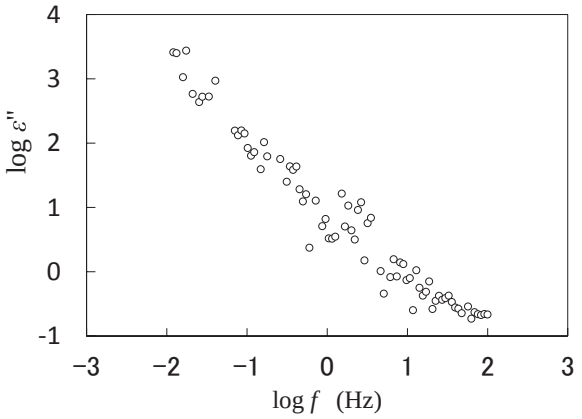

Fig. 2. Frequency dependence of loss permittivity for the p-PVC at 90 ° C

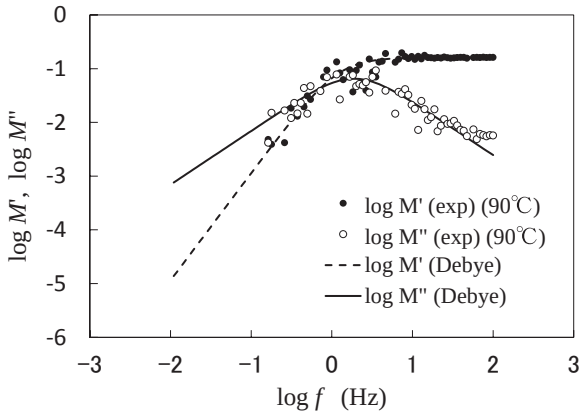

Fig. 3. Frequency dependence of electric modulus for the p-PVC at 90 ° C

In order to obtain a detailed information about the diversity of the ionic motion, the electric modulus M^* was calculated by the Eq.(1) as shown in Fig.3. Solid circles represent a real part of the electric modulus M' and open circles represent an imaginary part of the electric modulus M''. On the other hand, the dashed and solid lines are calculated values obtained by the Eq.(4). The former and the latter represent the real and imaginary parts of the electric modulus respectively as shown by the legend in Fig.3. In this analysis, the conductivity relaxation time is evaluated as 0.02s by using the Eq.(4). The experimental results are in good agreement with these lines. Therefore, a simple DC conduction characterized by a single conductivity relaxation time was observed. Consequently, it was confirmed experimentally that the long range ionic motion occurs under the homogeneous circumstance.

4.2. iPP

The frequency spectrum of the loss permittivity ε'' for iPP observed by BDS is shown in Fig.4. The loss permittivity increases with increase in frequency above about 100Hz. This increase is a lower frequency part of the α relaxation peak which should appears at a higher frequency [3]. The α relaxation is caused by the thermal motion of whole polymer molecule accompanied by an orientation motion of a dipole moment above the glass transition temperature of iPP which is about - 20 °C. This experiment was done at sufficiently higher temperature than the glass transition temperature. Additionally, in consideration of the observation of the α relaxation, the thermal motion of the polymer molecules in the non-crystalline part is so active that they make the enough free spaces for the ions to move. Therefore, the ions can move through the non-crystalline part even in the solid state.

On the other hand, the loss permittivity increases with decrease in frequency in the frequency range below about 10Hz to at least 0.001Hz as shown in Fig.4. This part of the plot seems to exhibit the characteristic of the DC conduction similar to p-PVC. Although a difference in the ionic motion between iPP and p-PVC is not clear from this plot, it will be clear by making analysis of the electric modulus.

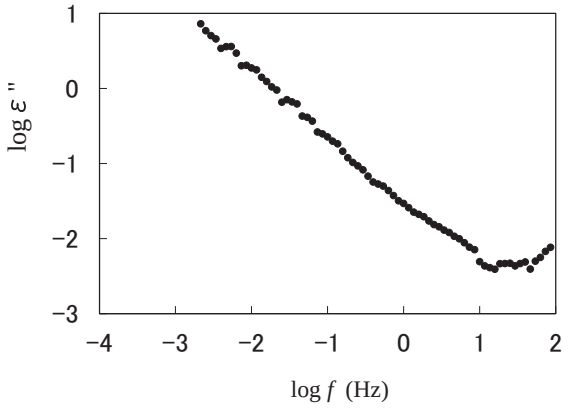

Fig. 4. Frequency dependence of loss permittivity for the iPP at 150 °C

The electric modulus was calculated by the Eq.(4) and the calculated result is shown in Fig.5 as a function of frequency. The real and imaginary parts of the electric modulus at the lowest temperature 90 °C is almost in agreement with the calculated curve obtained by the Eq.(4). However, a difference between the experimental and the calculated values grow with increase in temperature. Therefore, the

ionic motion observed higher temperatures is not characterized by the single conductivity relaxation time. The conductivity relaxation time is evaluated as 26.7s, 12.1s, and 1.7s respectively at the temperatures of 90°C, 110°C, and 150°C by using the Eq.(4). The values of the conductivity relaxation time decrease in ascending temperature. It is a reasonable result because the ion moves easily at a higher temperature. Those values are higher than that of p-PVC. This means that the ion in p-PVC is easy to move in comparison with the iPP. It can be interpreted as follows: The free space in the p-PVC is large because it is extended by the plasticizer.

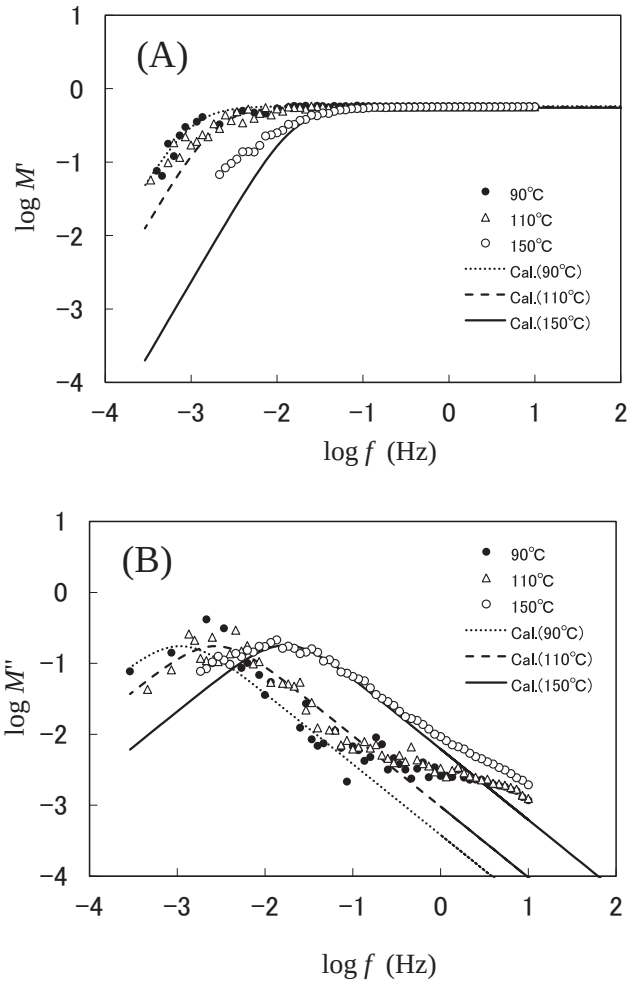

Fig. 5. Frequency dependence of electric modulus for the iPP at several temperature indicated in figure. (A) and (B) show the real and imaginary part of the electric modulus respectively

5. Discussion

The electric modulus of iPP was analyzed again in the assumption that the ionic motions are characterized by two conductivity relaxation times with different conductivity relaxation times. If the

electric modulus on a low frequency and a high frequency sides is represented by M_L^* and M_H^* respectively, the observed electric modulus is represented by a following equation,

$$M^* = M_L^* + M_H^* \tag{5}$$

Here, M_L^* and M_H^* are defined as follows,

$$M_k^* = M_{k,S} \frac{(\omega\tau_k)^2}{1+(\omega\tau_k)^2} + i M_{k,S} \frac{\omega\tau_k}{1+(\omega\tau_k)^2}, \quad (k = L, H) \tag{6}$$

Here, $M_{L,S}$, $M_{H,S}$, τ_L, and τ_H are the same physical meanings as those in the Eq.(4). The two conductivity relaxation times τ_L and τ_H characterize two kinds of ionic motion. A difference in the conductivity relaxation time in these ionic motions is considered to be caused by a variation of the free energy barriers impeding ionic motion [7].

The electric modulus at 150 °C which is the same data as shown in Fig.5 was analyzed by using the Eq.(6). The calculated values of the electric modulus by this analysis are shown in Fig.6 with the experimental data. The calculated values are in agreement with the experimental data. This result strongly suggests the existence of two kinds of ionic motion characterized by two conductivity relaxation times. The conductivity relaxation time is evaluated as τ_L=6.0s and τ_H=1.5s respectively for the lower and the higher frequency processes in Fig.6. The value of the higher frequency process τ_H=1.5s corresponds almost with the evaluated values 1.7s calculated in Fig.5. Therefore, the higher frequency process is considered to be the DC conduction caused by the similar free energy barriers to those of the lower temperatures' processes. On the other hand, the lower frequency process is considered to be a new process observed additionally.

Regarding the origin of this diversity of ionic motion, it is considered that a certain change occurs in polymer structure. In general, polymer molecules form a very thin platy shaped crystallite which is called lamella [3]. In the platy shaped crystallite, the polymer molecules extend against a direction to the wide surface of the plate. In case of iPP, the polymer molecules are in the form of a helical conformation inside of the crystallites. On the surface of the plate, the polymer molecule bends loosely or sharply and it reenters into the platy shaped crystallite (folded molecule). Additionally, some molecules do not reenter into their own crystallites but enter other crystallites across the non-crystalline part (tie molecule). Consequently, the non-crystallized part is composed of the loosely bended polymer molecules on the surface of the plate, the polymer molecules linking two crystallites, and the amorphous polymer molecules not joining in crystallites.

As explained in the section of the introduction, there are two possibilities for ion path. One is the inter-crystalline part and another is the inter-spherulute boundary. However, for the iPP, the former is highly possible from the discussion described below.

According to a study of phase transition of iPP [9-11], when a sample of iPP is cooled from the melt, it crystallizes as $\alpha 1$ form crystal. If the sample is heated continuously, the $\alpha 1$ form changes to a $\alpha 2$ form in the temperature range between 110 °C and 160 °C approximately. The transition temperature is different in depending on the sample preparation. The $\alpha 1$ to $\alpha 2$ form transition is interpreted as the disorder to order phase transition caused by a change of crystallized polymer conformation. This change of conformation is caused by an orientation of a methyl group of polypropylene. Namely, the $\alpha 1$ to $\alpha 2$ form transition is a metastable-stable transition [9].

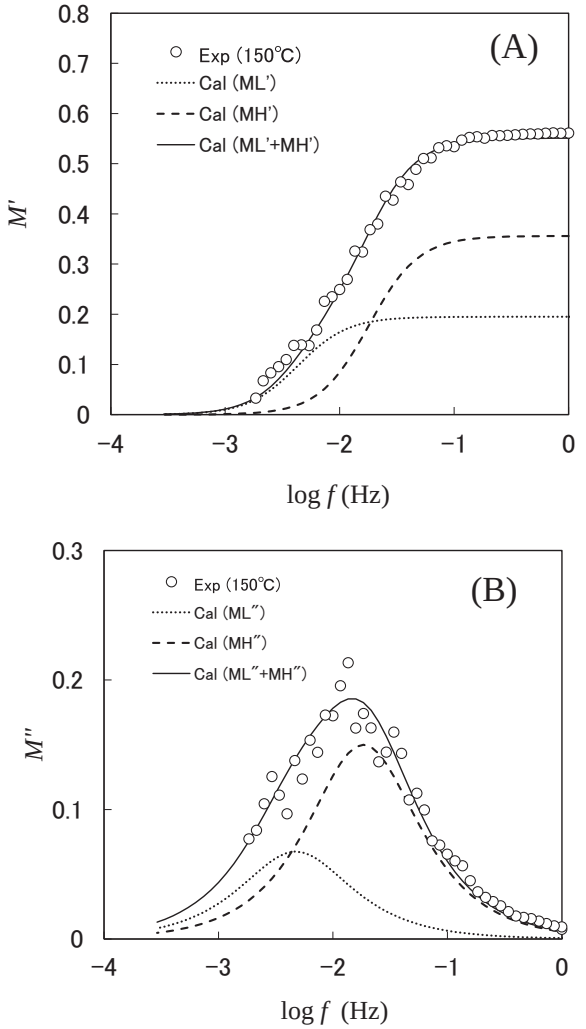

Fig. 6. Comparison between experimental and calculated values of electric modulus for the iPP at 150 ° C . (A) and (B) show the real and imaginary part of the electric modulus respectively.

The $\alpha 1$ to $\alpha 2$ form transition must accompany some sort of structural change in the non-crystalline part because some molecules composing the crystallite composes also the non-crystalline part. From a point of view of the free energy, this structural change in non-crystalline part affects the free energy barriers for ionic motion. As the plural processes of the ionic motion is caused by a variety of the free energy barriers [7], there is a strong possibility that the lower frequency process of the ionic motions appeared in Fig.6 are caused by the $\alpha 1$ to $\alpha 2$ form transition. As the results of the transition from the metastable $\alpha 1$ form to the stable $\alpha 2$ form, the free energy becomes larger near the folded molecules and the tie molecules in the non-crystalline part. Additionally, the conductivity relaxation time of the lower frequency process is larger than that of the DC conduction observed at the other temperatures. It may be caused by the partial increment of the free energy. As shown in Fig.5, a disagreement between the experimental and calculated values begins above 110 ° C . This result suggests that the additional ionic

motion begins to occur from this temperature. The correspondence between the temperature range of the change of ionic motion and the $\alpha 1$ to $\alpha 2$ form transition strongly supports the present speculation.

6. Conclusion

The relation between the electrical properties and the motion of residual ions was investigated for iPP and p-PVC. The loss permittivity and the electric modulus as a function of frequency were investigated in detail. Consequently, the DC conduction characterized by single conductivity relaxation time was observed for iPP and p-PCV. However, for the iPP, the additional process of ionic motion appears at higher temperatures. From the point of view of the $\alpha 1$ to $\alpha 2$ form transition, it is considered that the additional process of the ionic motion is accompanied by the structural change in the non-crystalline part caused by the the $\alpha 1$ to $\alpha 2$ form transition.

The speculation about the origin of the additional process of ionic motion seems to be reasonable, but it is not clear sufficiently in detail at the present stage. As this study is now at the starting point of this topic about iPP, further experimental and analytical research is necessary.

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